# AMMONIA-FREE NOx CONTROL SYSTEM

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**FOR JANUARY THROUGH MARCH 2004**


## Abstract

Research is being conducted under United States Department of Energy (DOE) Contract DE-FC26-03NT41865 to develop a new technology to achieve very low levels of NOx emissions from pulverized coal fired boiler systems by employing a novel system level integration between the PC combustion process and the catalytic NOx reduction with CO present in the combustion flue gas. The combustor design and operating conditions will be optimized to achieve atypical flue gas conditions. This approach will not only suppress NOx generation during combustion but also further reduce NOx over a downstream catalytic reactor that does not require addition of an external reductant, such as ammonia.

This report describes the work performed during the January 1 to March 31, 2004 time period.

## Table of Contents

## 1. Executive Summary

### 1.1 Project Overview

State-of-the-art NOx control technology for pulverized coal (PC) steam plants involves a combination of low NOx combustion and selective catalytic reduction (SCR) technologies. Development of these systems has approached a plateau and further improvements will likely be incremental. To advance NOx control technology to the next level, new concepts must be considered.

The objective of this project is to evaluate the viability of a novel integration between the PC combustion process and flue gas NOx reduction. The concept exploits the relationship between CO and NOx both in the combustion and flue gas NOx destruction processes to achieve very low levels of NOx from the boiler system without adding any external reductant, such as ammonia, typically used for SCR processes.

The project starts with a review and evaluation of existing NOx reduction and CO oxidation catalysts, including those catalysts formulations successfully used in the automotive applications, for their use in PC power plants. This knowledge, combined with prior catalyst research for power plant applications conducted at Lehigh University will allow the research team to identify and test catalyst formulations robust enough for power plant flue gas environments and which can achieve competitive NOx reduction performance and economic targets.

A detailed PC combustion study, applying computational fluid dynamics simulation program to performed boiler and burner design modeling, will complement the catalyst study by investigating ways to optimize the combustion process for the lowest NOx formation while generating sufficient levels of CO needed by the downstream catalytic NOx reduction process. Furnace configuration, air staging, and burner design will be optimized in this process.

The study will then focus on the comparative evaluation of a conceptual, 400 MWe, coal-fired PC boiler system, utilizing this novel NOx control concept. For this evaluation, the concept plant will be compared to a traditional PC boiler configured with current commercial low NOx combustion technology and an ammonia-based SCR system. The comparison will involve conceptual level design of the furnace and catalyst reduction system to obtain equipment pricing, operational costs, performance data as well as qualitative reliability information.

### 1.2 Progress During the Quarter

The project work during this quarter is focused on Task 1 – Catalyst Development and Selection and the preparation work for Task 2 – Catalyst Testing. The goal of task 1 is to select candidate catalysts for experimental characterization in Task 2. The work started with a detailed review of existing NOx reduction and CO oxidization catalysts for application in coal fired boilers, based on the following criteria: catalyst activity, deactivation, resistance to inhibitation / poisoning and cost.

The literature review of catalysts used in the NO destruction with CO as the reductant continued in this quarter. Specifically the work has been concentrated on several groups of potentially low cost, base metal catalyst for simultaneous NOx reduction and CO oxidation, including,

- Perovskite type minerals
- Copper oxide catalysts
- Cerium promoted copper oxides catalysts
- Hydrotalcite-based catalysts
- Carbon / char –based catalysts

Based on the comprehensive literature review, a short list of candidate catalysts was identified for Task 2 testing. The first group of test catalyst samples (activated carbon-based, metal oxides catalysts) have been prepared by aqueous incipient impregnation and ready for testing. The bench scale catalyst test rig has been inspected and restored to operational condition.

As of the end of this quarter, Task 1 - Catalyst Development and Selection- is completed, and Task 2 – Catalyst Testing - is ongoing at Lehigh University. We will continue the Task 2 work in the second quarter of 2004. We also will start working on Task 3 – Furnace Optimization.

## 2. Experimental

The experimental work during this quarter involves mainly procurement of catalyst raw material and lab supply, inspection and restoration of an existing test rig, and preparation of test catalyst. Detailed description of the test rig and catalyst preparation procedures will be included together with test results in the next quarterly report.

## 3. Results and Discussion

A summary of the literature reviews is given here. Detailed review and discussions are provided in the Appendix. Theoretically, there are two ways NOx can be reduced to nitrogen. The first is direct decomposition of NOx to $N_2$ and $O_2$. Studies of NOx decomposition catalysts have been reported. Catalysts considered include platinum group metals, transition metals exchanged zeolite and base metal oxides. Due to the slow reaction rate and the interference with oxygen and moisture in the flue gas, these studies have only limited success and direct decomposition catalysts have not been commercialized.

The second method is NOx reduction by reagent addition. The reagent can be ammonia, such as used in SNCR (high temperature ammonia injection) and SCR (low temperature reduction with catalyst). CO, $H_2$ and hydrocarbons have also been used as reductants. The catalysts studied for these reduction reactions include precious metals such as platinum, palladium, rhodium and base metal oxides or mix of metal oxides. This method has been successfully used in the automobile industry since the late 1970s. The so-called "Three-way Converter" (TWC) simultaneously reduces NOx, CO and HC emissions. The TWC is used in all passenger cars with conventional gasoline engines sold today in the US [1]. The catalyst is platinum or palladium and rhodium on ceramic or metal substrate. The CO functions as the NOx reductant over the rhodium surface according to the following reaction.

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad \text{(over metal catalyst)}$$

The excess CO and hydrocarbons are oxidized over the platinum/palladium surfaces. The TWC usually works in the 200 C to 500 C temperature range. A high NOx conversion up to 90-99% is achievable with this technology. The conventional gasoline engine runs at about stoichiometric conditions, controlled by fuel injection. Thus the flue gas will oscillate between slightly oxidizing and slightly reducing conditions at high frequency (usually one cycle in less than a second). Since continuous oxygen supply is needed for the CO and HC conversions, cerium

oxides, by its REDOX reaction between $Ce_2O_3$ and $CeO_2$, have been applied on TWC catalysts to regulate oxygen availability.

The automotive application shows that NOx control with CO as reductant is effective. However, automotive catalysts use mostly precious metals and may be cost-prohibitive for large-scale power plant application. Also, these catalysts are inhibited by high oxygen concentrations and poisoned by $SO_2$, both commonly found in power plant flue gas. Various mixed oxide catalysts have been considered for the in situ reduction of NO by CO in emission control, principally as a replacement for the noble metal based catalysts used in three-ways catalysts. Several groups of metal oxides of particular interest to this project have been reviewed and the following sections gives a summary for each of theses groups,

- Perovskite type minerals
- Copper oxide catalysts
- Cerium promoted copper oxides catalysts
- Hydrotalcite-based catalysts
- Carbon / char –based catalysts

## 3.1 Perovskite-type Catalysts

Perovskite oxide catalysts are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite, $CaTiO_3$. Perovskite are among the most abundant minerals on earth. The generic formula for perovskite is $ABO_3$ or $A_{1-x}C_xBO_3$, where the elements A, B, and C can be a large variety of different elements. Perovskite oxide catalysts exhibit high thermal stability but low surface areas. Perovskite materials can be active catalysts, especially if they are synthesized with additional components that enhance the redox properties of the $A_{1-x}C_xBO_3$ materials. The activity of the catalysts will then be strongly dependent on the reducing or oxidizing environment of the catalytic reaction of interest. The redox properties of the B cation are important and can determine the lability of the structural oxygen atoms. Since perovskite are relatively low-cost materials and can be both oxidation and reduction catalysts, they were proposed as automotive exhaust treatment catalysts.

Model studies have demonstrated that particular perovskite are active for the NO + CO reaction at moderate temperatures, e.g. as low as 300$^o$C under some conditions, and exhibit high selectivity for $N_2$ product formation at temperatures of 400$^o$C and higher. Most research on the reduction of NO with CO over perovskites has focused on the need to control NO and CO emissions from motor vehicles [3-6]. A successful catalyst must be designed to inhibit the promotion of $N_2O$, a greenhouse gas, while having an optimum concentration of adsorbed oxygen on the surface of the catalyst. Successful catalysts for this emission control reaction would preferably have high surfaces and maintain high activity and selectivity at low concentrations of NO and CO (ppm levels) in exhaust gases.

In general, the perovskite catalysts studied in the literature provide a wide temperature window for the reduction of NO. Experimental evidence indicates that the catalyst surface is first reduced by CO to create an oxygen vacancy, and then NO adsorption and dissociation occurs. The latter process takes place at a catalytic site consisting of a redox cation adjacent to the oxygen vacancy. The rate determining step can be the removal of the surface oxygen or the adsorption and dissociation of the NO reactant. Gas-phase components such as $O_2$, $CO_2$, and $H_2O$ can inhibit the overall CO + NO reaction by retarding the oxygen removal and by competitive adsorption on the catalyst surface. After dissociation of the NO molecule, rapid

mobility and removal of the oxygen is required for high, stable catalytic activity, which again is promoted by cations that readily undergo redox reactions and can function as oxygen transfer / storage components that depends on temperature and gas-phase composition. Examples of the latter active cations in the perovskite structure are Fe and Ce. At low reaction temperatures, $N_2O$ is a dominant product formed from NO, while at high reaction temperature, e.g. >350$^oC$, $N_2$ is the dominant or only nitrogen-containing product formed.

## 3.2 Copper Oxide Catalysts

Supported copper-based catalysts have been shown to exhibit relatively high NO conversion and $N_2$ selectivity under model laboratory conditions. It has been proposed that the high reactivity is correlated with the redox chemistry related to the Cu active site, although there is still controversy as to the oxidation state of the copper involved in the catalysis. Formation of $N_2O$ as a reaction product is related to low reaction temperatures. Addition of other redox promoters, e.g. Ce and Fe, to copper catalysts can enhance the NO reduction activity and/or $N_2$ selectivity.

Most of the studies indicate that the NO reduction reaction is produced by cations that readily undergo redox reactions. Additions of dopants that also can undergo redox reactions, e.g. Ce and Fe, have been shown to enhance the NO conversion and $N_2$ selectivity. The product selectivity is at least in part determined by the reaction temperature, where low reaction temperatures tend to favor $N_2O$ formation relative to the desired $N_2$ product. Gas-phase components such as $O_2$, $CO_2$, and $H_2O$ can inhibit the overall CO + NO reaction by competitive adsorption on the catalyst surface and by retarding oxygen removal from the surface of the catalyst. The presence of moisture inhibited the reaction by reversible competitive adsorption, while CO2 did not, and the presence of oxygen completely inhibited the reduction of NO. The reduction of NO only took place after all oxygen has been converted to $CO_2$, and therefore the NO reaction when oxygen was present required higher reaction temperatures, which also favored selectivity toward N2 and away from $N_2O$. However, depletion of CO in the reactant stream resulted in oxidation of the carbon support if excess oxygen were present, and NO was also reduced by the carbon support, which was oxidized, at temperatures >327oC. Upon extensive analysis and characterization, it was concluded that highly dispersed Cu2+ species on Al2O3 were the active sites for selective reduction of NO to N2, while aggregated Cu species preferentially oxidize CO without reducing NO. Upon increasing the Cu content of the catalysts, it was shown that the increasing presence of aggregated Cu species drastically reduced the NO conversion and N2 formation capability, while reducing the reaction temperature at which $N_2O$ was formed and CO was oxidized.

## 3.3 Cerium Promoted Catalysts and Hydrotalcite Group

Supported copper-based oxide catalysts have been shown to exhibit high NO conversion and $N_2$ selectivity under model laboratory conditions. It has also been demonstrated that adding Ce to Cu-based catalysts can enhance the NO reduction activity and/or $N_2$ selectivity. The Ce promoter also provides a synergetic effect with the Cu in providing tolerance of the catalyst for the presence of $O_2$, $H_2O$, and $SO_2$ in the NO + CO reactant stream. Thus, the Ce/Cu couple inhibits deactivation induced by poisons. It has been proposed that effect results from enhancing redox couples so that redox reactions involving Cu and Ce are promoted and occur more easily and at lower temperatures. At the same time, selectivity to the $N_2$ deep reduction product of NO is promoted, which is important since the formation of undesirable $N_2O$ as a reaction product tends to be favored by low reaction temperatures. High dispersions of the active sites are required, and it has been reported that formation of ternary oxide catalysts through a hydrotalcite-type

intermediate, based on the structure found in nature for $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, provides high dispersions of active components.

It is well established that cerium oxide is a beneficial additive to three-way automotive catalysts. Its attributes include stabilization of alumina supports against sintering, increased dispersion of noble metals, promotion of the water gas shift reaction. To study the synergism between Cu and Ce in oxides, catalysts consisting of (a) CuMgAlO, (b) CeMgAlO, and (c) CuCeMgAlO were synthesized by a co-precipitation method. The presence of both Cu and Ce in the catalyst resulted in a highly dispersed, active, stable, and poison-resistant catalyst for the reduction of NO by CO. It was proposed that Cu and Ce together gives a high concentration of $Cu^{1+}$ species and oxygen vacancies that function as adsorption sites and promotes the water gas shift reaction, as well as the NO reduction reaction. The $SO_2$ tolerance of the (c) CuCeMgAlO catalyst was the most interesting result.

It has been shown that ternary component catalysts, e.g. Cu/Zn/Al and Cu/Zn/Cr used for methanol synthesis from syngas, one of the largest industrial processes today, catalysts with the "proper" composition and formed *via* a hydrotalcite-type intermediate appears to yield the most active and highly dispersed catalysts. A variety of hydrotalcite-type materials, including Cu/Co/Al and Cu/Mg/Al, have been prepared as catalysts for the reduction of NO by CO. Catalysts prepared through a hydrotalcite-type precursor were more activity for NO reduction than catalysts prepared by stoichiometrically co-precipitated samples and materials prepared by mechanically mixing the metal oxides prior to calcination. It was shown that calcinations at 350-400$^oC$ gave more active catalysts than those calcinations at 600 or 800$^oC$. It was that the most reducible catalyst, Cu/Co/Al, was the best catalyst for reduction of NO by CO. It is clear that once again, surface redox chemistry is crucial to the performance of the catalyst and that oxygen transfer and removal from the surface of the catalyst can be limiting reaction step.

### 3.4 Carbon Based Catalysts

Activated carbon and other carbons have been investigated as direct reducing agents, as well as providing high surface area supports for alkali and transition metal catalysts, for NO reduction. Carbons do directly reduce NO, and different reactions are dominant in different temperature regimes. Under some reaction conditions, the presence of $O_2$ in the reactant mixture promotes NO reduction, while the presence of moisture tends to inhibit the reaction, particularly by competitive adsorption at lower reaction conditions.

Highly activated materials that have been pyrolyzed usually require appreciably higher temperatures for NO reduction, even when catalysts are impregnated into the carbons. However, dispersed metal catalysts tend to enhance higher NO reduction at lower temperatures over most carbons, as well as higher carbon burnoff. High dispersions of the active sites are required, preferably on the surface of high surface area carbons. The presence of CO in the reactant gas mixture aids in the reduction of NO, again in a temperature dependent manner. The simultaneous presence of catalysts on carbon supports and CO in the reactant gas mixture can greatly promote the reduction of NO in a gas stream.

#### 3.4.1 Carbon Reduction of NO

Various carbons have been investigated as a reducing medium for NO conversion to $N_2$. The carbon is the reducing agent and is consumed in the reduction of NO. Carbons and chars can

naturally contain other moieties such as alkali/alkaline earth metals and transition metals usually in an oxidized or sulfided state. It is sometimes difficult to separate the effects of carbons in reducing NO from the effects of catalysts. It was observed that the presence of CO enhances the reduction of NO. The CO might fulfill two roles in NO reduction; (A) removing surface oxides from the carbon surface, C(O), to expose free reactive carbon sites, C*, and (B) direct reduction of the NO by reaction, i.e.

(A) $CO + C(O) \rightarrow CO_2 + C^*$

(B) $2CO + 2NO \rightarrow 2CO_2 + N_2$.

With respect to other gases in the reactant stream, it has been reported that the NO-carbon reaction is inhibited by the presence of water vapor. On the other hand, the presence of oxygen enhances the rate of NO reduction, especially in the presence of catalysts in the carbons.

### 3.4.2 Reduction of NO by Catalyst-Promoted Activated Carbons

A large amount of studies was related to catalyst-promoted activated carbons. Example of doping the coal-derived carbon with $K^+$, *via* $CH_3COOK$, or KOH, by ion exchange or by impregnation, promotion of significant reduction of NO was found to occur at considerably lower temperatures. Three characteristic reactivity regions were found. Potassium was found to be very active in dissociating NO, even at temperatures as low at 60°C. It was proposed that this is due to $K^+$ being reduced by the carbon substrate and promotion of surface redox reactions. The effects of $K^+$ on NO reduction over five coal-derived chars were examined, where the chars were obtained from two lignites, two subbituminous, and one hvA bituminous coals. The most active coal chars for NO reduction were obtained by pyrolysis at 900°C followed by treatment with aqueous KOH using a KOH/coal wt ratio of 0.5/1.0.

A study of monometallic K, Fe, Co, Ni, and Cu catalysts on activated carbon was subsequently carried out. The activated carbon was prepared from a hvA bituminous coal and impregnated with aqueous KOH. It was reported that the metal catalysts were ineffective at temperatures lower than about 200°C. However, at higher temperatures all of the metals catalyzed the NO reduction reaction, and the total activity was the result of two factors, the tendency of the metal to be oxidized by NO and the easiness of the resulting oxide to be reduced by carbon. The Cu and Co catalysts exhibited the highest NO conversion at 300°C and the lowest temperatures for significant NO reduction to be observed. However, these two catalyst exhibited the highest burnoff of carbon at 300°C, some 2-3 times higher than observed for the Ni, Fe, and K catalysts. However, the latter three catalysts exhibited lower NO reduction levels than the Cu and Co catalysts. The effect of Fe, as well as Na and Ca, on coal chars was studied too.

Portions of the same coal-derived activated carbon were also impregnated with excess aqueous solutions of Cr, Fe, Co, Ni, and Cu nitrates. All of the transition metals catalyzed the NO-carbon reaction (studied in the absence of $O_2$), causing a decrease in the activation energy and substantial shifts of the NO reduction curves toward lower temperatures. The TPR curves support a redox mechanism involving different oxidation states of the metals and the carbon matrix. At low reaction temperatures (<400°C), Fe, Co, and Ni are the most effective catalysts, which is consistent with their abilities to chemisorb NO dissociatively. At high reaction temperatures (500°C), Cu, Co, and Ni exhibit the highest activities. These observation indicate that at low temperatures, the controlling step in the process is NO chemisorption, whereas at high temperatures reduction of the intermediate oxidized metal species is the rate-limiting step in the reaction sequence. At low reaction temperatures, all of the transition metals were much less active in promoting the NO-carbon reaction than was K (in terms of mol NO reduced/mol of

metal/sec). However, at 500°C the Cu catalyst was more reactive than the K catalyst, and Co and Ni were approaching the activity of the K promoter. It was pointed out that the K catalyst showed a high NO removal capability at about 200°C and achieved 100% NO reduction at 500°C. The transition metal catalysts exhibit differing behaviors because of their difference redox properties. At low temperatures, catalyst deactivation is observed because of oxygen accumulation on the surface. For the catalysts, the transfer of oxygen from the oxidized catalytic site to the carbon is proposed to be crucial for maintaining high steady-state catalytic activity.

More recently, deposition of bimetallic catalysts on carbon supports and model studies of NO reduction by the carbon have been carried out. It was found that all of the transition metals promoted the K-carbon system and exhibited a synergetic effect, in particular the temperature for NO reduction was reduced, i.e. to the 200-250°C range, and the $N_2$ selectivity was nearly 100%. Among the metals analyzed, it was stated that the K-Ni catalyst was the most interesting because it combined a high NO reduction activity at low temperatures with the lowest loss of carbon by combustion. The bimetallic catalysts, K-Ni, Ni-Co, and Ni-Cu, promoted NO reduction too. The Ni-Cu catalyst was reported to yield the best performance at 250°C by showing a high NO conversion and selectivity, high $N_2$ product selectivity, and absence of $N_2O$ and CO in the reaction products.

As a summary, carbons are active support materials for the reduction of NO in gas streams. Without the presence of catalysts, operation temperatures are higher than 500°C. However, supporting base metal catalysts and/or redox transition metal catalysts in mono, bi or ternary metal forms on the carbon supports reduced the temperature required for NO reduction. The thermal treatment in obtaining the activated carbon or char can greatly affect the temperature that is needed to obtain significantly high levels of NO reduction. The presence of CO and O2 in the reactant stream both promotes the reduction of NO. In addition, the simultaneous presence of catalysts on carbon supports and CO in the reactant gas mixture can greatly promote the reduction of NO in a gas stream.

## 4. Conclusion

Task 2 of the project is ongoing. No technical conclusions are currently available.

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## Appendix - Literature Review on Catalytic Reduction of NO by CO

### Part-1A

**Part 1A** is a series of reviews centered on different types of catalysts that could be utilized for the *in situ* reduction of NO by CO in flue gases, i.e. $2CO + 2NO \rightarrow N_2 + 2CO_2$. Perovskite oxide catalysts exhibit high thermal stability but low surface areas. Model studies with relatively high concentrations of NO and CO, e.g. 0.1-5% in an inert gas stream, have demonstrated that particular perovskite are active for the NO + CO reaction at moderate temperatures, e.g. as low as 300°C under some conditions, and exhibit high selectivity for $N_2$ product formation at temperatures of 400°C and higher. Successful catalysts for this emission control reaction would preferably have high surfaces and maintain high activity and selectivity at low concentrations of NO and CO (ppm levels) in exhaust gases. Pertinent references are reviewed here and more detailed conclusions are given at the end of the review. Copies of the most pertinent reference papers are included with this review.

A. *Perovskite-Type Oxide Catalysts.* Perovskite-type materials are based on the structure of a multi-component natural mineral, i.e. $CaTiO_3$, having a generic formula of $ABO_3$ or $A_{1-x}C_xBO_3$, where the elements A, B, and C can be a large variety of different elements. Simple perovskite can be easily synthesized, include $SrTiO_3$, $BaTiO_3$, $LaFeO_3$, $BaCeO_3$, and $SrFeO_3$. In these materials with A being a divalent cation, the B element is stabilized in octahedral sites as $B^{4+}$ between close-packed $AO_3$ layers. This can be visualized as A being on the eight corners of a cube, with $B^{4+}$ in the center of the cube and the six oxygen atoms being in the middle of the six faces of the cube, giving $O_h$ or distorted $O_h$ symmetry to the $B^{4+}$ cation. As the sizes of A and B change, distortion of the unit cell can occur by displacement of cation B and the oxygen anions relative to the A cations on the corners of the cube structure, which changes the properties of the material. These $ABO_3$ materials tend to be very thermally stable, but the stability is related to the fitting of the B element to the size of the octahedral site (hole) between the $AO_3$ layers. As an example, $Ti^{4+}$ with an ionic diameter of 1.21 A (0.121 nm) gives a very stable $BaTiO_3$ material [$BaO_{(s)} + TiO_{2(s)} \rightarrow BaTiO_{3(s)}$ with $\Delta H = -163$ kJ/mol], but $Ba(B)O_3$ materials with B cations of larger diameter tend to be less stable [1]. These materials can be synthesized by grinding the solid oxides together and calcining at temperatures above 900°C (usually repeated a number of times), and thus they are stable in oxygen-containing atmospheres at these high temperatures.

Perovskite materials can be active catalysts, especially if they are synthesized with additional components that enhance the redox properties of the $A_{1-x}C_xBO_3$ materials. Here C is approximately the same size as A or B, partially substituted for either A or B, but has a different valence state than the cation for which it was substituted. This induces a non-stoichiometry in the oxygen content of the material. The activity of the catalysts will then be strongly dependent on the reducing or oxidizing environment of the catalytic reaction of interest. The redox properties of the B cation are important and can determine the liability of the structural oxygen atoms. Since perovskite are relatively low-cost materials and can be both oxidation and reduction catalysts, they were proposed as automotive exhaust treatment catalysts [2]. An early study of perovskite systems as catalysts for the NO + CO reaction classified the reaction on these catalysts as an intrafacial process involving surface oxygen from the perovskite lattice [3]. It was reported that the reduction of NO proceeds *via* $N_2O$ as an intermediate, whose formation was favored on reduced perovskite surfaces but depressed on oxidized surfaces.

Since that study, most research on the reduction of NO with CO over perovskite has focused on the need to control NO and CO emissions from motor vehicles [4-7]. Many of the laboratory studies have focused on perovskite materials having the general formula of $La_{1-}$

$_xSr_x(Fe^{3+}/Fe^{4+})O_{3\forall y}$ [4,6-8] or $La_{1-x}Ce_x(Co^{n+})O_{3\forall y}$ [9-12], with goals of understanding the oxygen release/uptake as a function of composition and the role of metal cation oxidation state in the activity of the catalysts for NO reduction with CO. It has been reported [4,6] that the following sequence of surface reaction steps occurs for the overall reaction to achieve the reaction of NO with CO:

$NO_{(g)}$ 6 $NO_{(ads)}$ (1)

$NO_{(ads)}$ 6 $N_{(ads)}$ + $O_{(ads)}$ (2)

$CO_{(g)}$ 6 $CO_{(ads)}$ (3)

$CO_{(ads)}$ + $O_{(ads)}$ 6 $CO_{2(g)}$ (4)

$N_{(ads)}$ + $NO_{(ads)}$ 6 $N_2O_{(ads)}$ (5)

$2N_{(ads)}$ 6 $N_{2(g)}$ (6)

$N_2O_{(ads)}$ 6 $N_{2(g)}$ + $O_{(ads)}$ (7)

$2O_{(ads)}$ 6 $O_{2(g)}$. (8)

The net desired reaction is complete reaction of the reactants, i.e.

$2CO + 2NO$ 6 $N_2 + 2CO_2$ (9)

It is noted that a successful catalyst must be designed to inhibit the promotion of $N_2O$, while having an optimum concentration of adsorbed oxygen on the surface of the catalyst. The oxidation states of the A, B, and C cations in perovskite can promote or inhibit the reactive of surface lattice oxygen and adsorbed oxygen species from NO, which creates an oxygen-rich or oxygen-poor surface *via* Step 8 that influences the preceding reaction steps.

With a $LaCoO_3$ catalyst, steady state isotopic transient kinetic analysis experiments were carried out in which the isotopic switches of $^{12}CO$ to $^{13}CO$ or $^{14}NO$ to $^{15}NO$ were performed after the CO + NO reaction reached steady state at different temperatures [9]. The results (with CO = NO = 1-5% in carrier gas) were consistent with two dominant reactions occurring over the catalyst, the extent of each being dependent on the reaction temperature. The high temperature reaction, e.g. at 700$^o$C, is represented by Equation 9, while the low temperature reaction, e.g. at 300$^o$C, is represented by Equation 10.

$2CO + 2NO$ 6 $N_2 + 2CO_2$ (9)

$2NO + CO$ 6 $N_2O + CO_2$ (10)

At 300$^o$C, 0% $N_2$ was observed in the products, while at 700$^o$C, 0% $N_2O$ was observed as a product [9]. At moderate temperatures, the results were consistent with $N_2O$ being an intermediate for the formation of $N_2$. However, at high temperatures a different pathway might lead directly from NO to $N_2$.

For $La_{1-x}Ce_x(Co^{n+})O_{3\forall y}$ catalysts using a reactant mixture of NO = CO = 1% in carrier gas at 200-450$^o$C [10] or with NO = CO = 3500 ppm in the temperature range of 220-650$^o$C [11], the sequence of reactions 10 and 9 were observed. It was reported that the initial adsorption of NO is enhanced by oxygen vacancies on the surface of the catalyst [12], which could occur by oxidation of CO by the catalyst (Equations 3 and 4) or by thermal desorption of lattice oxygen from the surface (Equation 8) [8]. This is followed by dissociative adsorption of NO on the surface (Equations 1 and 2), which replaces the missing lattice oxygen. The adsorbed N species can then react via Equations 5 and 6 to form $N_2O$ and $N_2$ or with CO to form adsorbed NCO (represented by Equation 11).

$N_{(ads)}$ + $CO_{(g\ or\ ads)}$ 6 $NCO_{(ads)}$ (11)

In the catalysts being discussed, the B atom in the perovskite structure can undergo a redox reaction to some degree, e.g. thermal desorption of oxygen from the surface, i.e.

$8SrFe^{4+}O_3$ 6 $O_2 + 6SrFe^{4+}O_3 + 2SrFe^{3+}O_5$ [8] (12)

$Co^{3+}/O_2^-$ 6 $O_2 + Co^{2+}$ [10] (13)

or reaction of lattice oxygen (e.g. $O^{2-}$ = Co!O!Co) with CO to give $CO_2$ as pointed out above. This indicates that the strength of the redox metal-to-oxygen bond will be important in the activity of the catalyst and that gas phase oxygen could be an inhibitor for the NO + CO reaction. Indeed, considering NO decomposition, it has been stated that "it is well-known that coexisting gaseous oxygen causes a decrease in the activity of almost all the NO decomposition catalysts", and this inhibition effect was shown for both $O_2$ and $CO_2$ over $La_{0.8}Sr_{0.2}CoO_3$ [13].

While it was found that the $LaMnO_{3+y}$ catalyst has the highest activity of the first row transition metal perovskite catalyst for the total oxidation of CO [14], it was reported that partial substitution of the La by Sr in these catalysts, i.e. $La_{1-x}Sr_xBO_3$ where B = first row transition metal, significantly affects oxidation activity [15]. In studying the NO + CO reaction over transition metal-containing perovskite, the $LaFeO_3$ catalyst was observed to have the highest activity for NO reduction from a NO = CO = 1500 ppm in He reactant stream, i.e. >90% reduction at 350°C [16]. Substitution of Sr for part of the La, e.g. $La_{1-x}Sr_xBO_3$ where x = 0.3 or 0.5, decreased the activity of the $LaFeO_3$ catalyst but increased the activity of the other transition metal-containing catalysts. However, the $LaFeO_3$ catalyst was still more active for NO reduction by CO than any of the substituted catalysts [16].

While other perovskite have been studied for this and other catalytic reactions, as can be found in the citations in the references given here, a particularly informative study [17] was carried out with the following multi-substituted catalysts:

1. $La_{1-y}Ce_yFeO_3$ (y = 0.2-0.5)
2. $La_{1-x}Sr_xFeO_3$ (x = 0.2-0.5)
3. $La_{1-x-y}Sr_xCe_yFeO_3$.

It was found that high NO conversions from a NO/CO/He = 2/2/96% reactant mixture were favored by the presence of cerium in the catalysts and that those catalysts contained $CeO_2$ and alpha-$Fe_2O_3$ (detectable by X-ray powder diffraction) as well as the $LaFeO_3$ and $SrFeO_{3-x}$ perovskite phases. The doubly substituted $La_{1-x-y}Sr_xCe_yFeO_3$ catalysts containing both Sr and Ce were usually the most active of the catalysts tested, although the activity and selectivity of the $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ and $La_{0.7}Ce_{0.3}FeO_3$ catalysts were nearly identical, reaching about 50% NO conversion at 400°C and 100% $N_2$ selectivity at 440-460°C (and higher temperatures). At lower reaction temperatures, $N_2O$ was also a reaction product that progressively decreased as the temperature was increased. It was proposed that there was a synergistic behavior of the $CeO_2$ and the $SrFeO_{3-x}$ perovskite components based on oxidation-reduction cycles, accompanied by enhanced desorption of product $CO_2$ from the catalyst, i.e. weaker chemisorption of $CO_2$ to block the active sites on the catalyst [17].

Considering perovskite catalysts that exhibit high thermal stability, the NO + CO reaction involves both oxidation and reduction processes that occur at moderate temperatures. However, these catalysts provide a wide temperature window for the reduction of NO. Experimental evidence indicates that CO to create an oxygen vacancy, and then NO adsorption first reduces the catalyst surface and dissociation occurs. The latter process takes place at a catalytic site consisting of a redox cation adjacent to the oxygen vacancy. The rate determining step can be the removal of the surface oxygen or the adsorption and dissociation of the NO reactant. Gas-phase components such as $O_2$, $CO_2$, and $H_2O$ can inhibit the overall CO + NO reaction by retarding the oxygen removal and by competitive adsorption on the catalyst surface. After dissociation of the NO molecule, rapid mobility and removal of the oxygen is required for high, stable catalytic activity, which again is promoted by cations that readily undergo redox reactions and can function as oxygen transfer/storage components that depends on temperature and gas-phase composition. Examples of the latter active cations in the perovskite structure are Fe and Ce. At low reaction temperatures, $N_2O$ is a dominant product formed from NO, while at high reaction temperature, e.g. >350°C, $N_2$ is the dominant or only nitrogen-containing product

formed. Perovskite catalysts typically are well-defined materials, have high thermal stabilities, and possess low surface areas (5-20 $m^2/g$) that yield low turnover frequencies for the active sites.

**Part-1B**

**Part 1B** is a series of reviews centered on different types of catalysts that could be utilized for the *in situ* reduction of NO by CO in flue gases, i.e. 2CO + 2NO 6 $N_2$ + $2CO_2$. Supported copper-based catalysts have been shown to exhibit relatively high NO conversion and $N_2$ selectivity under model laboratory conditions. Recent research on copper catalysts is reviewed, and it is proposed that the high activity is correlated with the redox chemistry related to the Cu active site, although there is still controversy as to the oxidation state of the copper involved in the catalysis. Formation of $N_2O$ as a reaction product is related to low reaction temperatures. Addition of other redox promoters, e.g. Ce and Fe, to copper catalysts can enhance the NO reduction activity and/or $N_2$ selectivity. Pertinent references are reviewed here and more detailed conclusions are given at the end of the review. Copies of the most pertinent reference papers are included with this review.

B. *Copper Oxide Catalysts*. Early research in the reduction of NO and the oxidation of CO over metals and metal oxide catalysts was driven by the need to reduce or eliminate the emissions of these pollutants from automobiles. This was accompanied by the need to reduce the emissions from industrial sources of pollutants that contribute to acid rain, i.e. $SO_2$ and NO. NO from both sources reacts in the atmosphere to form ozone, a major component of smog and a photochemical oxidant. Automotive catalysts tended to be based on noble metals (oxygen-poor working environment), while catalysts for stationary industrial applications tended to be based on metal oxides (oxygen-rich working environment). The early research on catalyst development has been reviewed and updated elsewhere [1-5], and this review will concentrate on recent research studies.

Many types of metal oxide catalysts have been investigated for activity for the reduction of NO by using CO as the reducing agent. Driving forces for this were (and are) (1) the largest use of Rh is as the active (and expensive) component in automotive catalysts for NO reduction and replacement by a base metal oxide catalyst would greatly reduce the cost of the catalytic converter and (2) supported vanadia is the active component in catalysts for stationary industrial applications that use ammonia injection into the exhaust gas stream to achieve selective catalytic reduction (SCR) of NO, where exhaust gases are relatively rich in oxygen, but it has a relatively high (350-450$^oC$) and narrow operation temperature, is poisoned by alkali, and is an environmentally hazardous material (and hazardous waste upon reactor discard) and replacement by a base metal oxide would be economically and environmentally beneficial. In many stationary applications requiring NO abatement, as in mobile emission reduction, CO is the major reducing species present in the exhaust gas, and it is highly desirable to utilize this reducing agent for *in situ* reduction of NO to $N_2$. This section of the report will focus on research carried out with simple copper oxide catalysts as NO reduction catalysts using CO as the reductant.

In 1993, Cu-Cr oxide catalysts supported on porous carbon (surface area = 1200 $m^2/g$) were prepared, and it was reported that the catalysts were active for both NO reduction and CO oxidation [6]. At low temperature and low NO conversion levels from reactants mixture containing 2000 ppm NO, the NO reduction reaction was completely selective to $N_2O$, represented overall by Equation 1. At higher temperatures, the selectivity switched to $N_2$, represented by Equation 2.

$$2NO + CO \text{ 6 } N_2O + CO_2 \quad (1)$$

$$2NO + 2CO \text{ 6 } N_2 + 2CO_2 \quad (2)$$

The rate-determining step is probably the dissociation of NO on the catalyst. The presence of moisture inhibited the reaction by reversible competitive adsorption, while $CO_2$ did not. The presence of oxygen completely inhibited the reduction of NO. The reduction of NO only took place after all oxygen has been converted to $CO_2$, and therefore the NO reaction when oxygen was present required higher reaction temperatures, which also favored selectivity toward $N_2$ and away from $N_2O$. However, depletion of CO in the reactant stream resulted in oxidation of the carbon support if excess oxygen were present, and NO was also reduced by the carbon support, which was oxidized, at temperatures >327°C.

To probe the oxidation state of copper that plays a part in the catalytic reduction of NO by CO, a CuO/gamma-$Al_2O_3$ catalyst was prepared and analyzed by *in situ* X-ray absorption near-edge structure spectroscopy (XANES) [7]. The initial 2.1 wt% Cu/$Al_2O_3$ catalyst contained two $Cu^{2+}$ species. Upon testing in NO = CO = 2 vol% in He and sequentially increasing the reaction temperature, CO began to reduce the $Cu^{2+}$ species at about 325°C to form $Cu^{1+}$. At the same time, the NO conversion curve exhibited light-off, and the NO reduction level ran approximately parallel to the increasing concentration level of $Cu^{1+}$ to about 475°C, at which temperature all of the $Cu^{2+}$ had been converted to $Cu^{1+}$. Therefore, it was concluded that (a) the $Cu^{1+}$ species was involved in the slow rate step of reaction, (b) was generated by CO reduction of $Cu^{2+}$ species, and (c) was oxidized by the NO dissociation/reduction reaction. A redox reaction scheme was proposed in which the NO dissociation step was the slow step of the reaction. It was also pointed out that the formation of $Cu^{1+}$ preceded NO conversion, which was consistent with CO being more strongly adsorbed onto the $Cu^{1+}$ sites than was NO. It was pointed out that upon complexation, CO presents strong covalent sigma(s)-donation and pi(p)-back-donation contributions to the adsorption bond and an energy about four times greater than of NO coordination [7]. Therefore, higher reaction temperatures, e.g. >425°C, significantly enhance the rate of the slow reaction step, i.e. NO adsorption and dissociation on $Cu^{1+}$ species.

In contrast to the above study, a $La_2CuO_4$ catalyst that was synthesized and tested for the NO/CO reaction was found to be reduced to $Cu^o$-$La_2O_3$ after testing [8]. The study concluded that "it seems that metallic Cu species are the most active sites for the CO + NO reaction" [8].

The adsorption chemistry of NO and CO on supported copper species has been briefly reviewed by Hadjiivanov and Kn¯zinger, and they carried out addition IR studies with a 1 wt% Cu/$SiO_2$ (Aerosil) catalyst [9]. With respect to CO and NO adsorption, they summarized as follows:

| Copper State | CO Bonding | Infrared Band ($cm^{-1}$) |
|---|---|---|
| $Cu^+$ | Sigma and Pi Backbonding | 2160, 2130, mainly 2130-2135 |
| $Cu^{2+}$ | Mainly electrostatic forces & weak sigma bonding | 2150-2236, mainly 2200-2208 |
| $Cu^O$ | Pi-bonding (weak, unstable) | 2080-2110 |

| Copper State | NO Bonding | Infrared Band ($cm^{-1}$) |
|---|---|---|
| $Cu^+$ | Weak Pi Backbonding | 1740-1820 |
| $Cu^{2+}$ | Stronger Sigma Bonding | 1845-1964, e.g. 1882 |
| $Cu^O$ | (Not formed?) | |

It was concluded [9] that

(a) CO-$Cu^{2+}$ is stable at low temperature or under CO pressure
(b) NO-$Cu^{2+}$ is more stable that CO-$Cu^{2+}$ and NO can replace CO on the $Cu^{2+}$ center
(c) CO-$Cu^{1+}$ is stable
(d) NO-$Cu^{1+}$ is unstable (doesn't form)

(e) CO-$Cu^o$ stability is between that of CO-$Cu^{1+}$ and CO-$Cu^{2+}$.

In addition, small amounts of $O_2$ added to the CO-NO-Cu/$SiO_2$ system causes oxidation of the $Cu^{1+}$ sites to $Cu^{2+}$ sites and leads to formation of surface nitrates that block the $Cu^{2+}$ sites for NO adsorption.

The effect of oxygen in the CO-NO reactant mixture has been further studied using a 0.5 wt% Cu/gamma $Al_2O_3$ catalyst, which was selected as the best catalyst from a variety of catalysts tested [10]. Using a reactant gas mixture of 1% NO, 1% CO, and 0.5% $O_2$ in Ar at 500°C, about 15% of the NO was reduced with very high selectivity to $N_2$ while 100% of the CO was converted. At 450°C, the NO conversion was twice as high, with the $N_2/N_2O$ selectivity being 1/1 (still with 100% CO conversion). At 300°C, the NO conversion had dropped to about 25% of that observed at 450°C, the selectivity was nearly 100% to $N_2O$, while the CO conversion had dropped to approximately 20%. Upon extensive analysis and characterization, it was concluded that highly dispersed $Cu^{2+}$ species on $Al_2O_3$ were the active sites for selective reduction of NO to $N_2$, while aggregated Cu species (perhaps CuO/$Cu^o$) preferentially oxidize CO without reducing NO. Upon increasing the Cu content of the catalysts, it was shown that the increasing presence of aggregated Cu species drastically reduced the NO conversion and $N_2$ formation capability, while reducing the reaction temperature at which $N_2O$ was formed and CO was oxidized [10].

With a 2% copper catalyst supported on silica-pillared layered niobate (Cu/Si-$Nb_3O_8$), it was shown that pretreatment of the catalyst with steam or adding 2% steam into a CO/NO reactant mixture increased the activity of the catalyst for NO reduction [11]. The presence of the steam only decreased the product selectivity to $N_2$ slightly.

Syntheses of Cu/$Al_2O_3$-$TiO_2$ catalysts under gelling conditions at various pH values were carried out. It was reported that the catalyst prepared at pH 9 exhibited the lowest light-off temperature for NO reduction by CO [12]. Analyses showed that the catalyst had the highest $Cu^o$ / ($Cu^{1+}$ + $Cu^{2+}$) ratio of those prepared and tested.

An Ambersorb 572 resin was utilized as a support for transition metal oxides in a screening study for the reduction of NO by CO at low temperature [13]. The catalysts were prepared by incipient wetness impregnation of metal nitrates, which were decomposed by calcinations at 360°C in flowing He. The catalytic studies were carried out with 5% NO + 10% CO in He at a low GHSV = 60 $hr^{-1}$. Over a 5 wt% CuO/Ambersorb catalyst, it was observed that the NO was completely converted to $N_2$ (79%) and $N_2O$ (21%) at 180°C. Supported NiO and $Ag_2O$ catalysts exhibited lower activity and $N_2$ selectivity. Analogous Mn and Co catalysts exhibited lower activity, required higher reaction temperature, and still produced an appreciable quantity of $N_2O$. Addition of 1% $CeO_2$ to the CuO catalyst improved the $N_2$ selectivity to 99% at 180°C. The effect of Ce doping on Cu-based catalysts is significant, has been more intensively studied, and will be discussed further in another report.

A 5% CuO/5% $Fe_2O_3$/Ambersorb catalyst was also tested for NO reduction with CO using the same reactant concentrations but with GHSV = 300 $hr^{-1}$ [13]. The addition of Fe decreased the activity of the catalyst, but increasing the reaction temperature to 220°C resulted in 100% NO reduction to $N_2$. Addition of 5 vol% $O_2$ to the reactant stream resulted in a decrease in NO conversion, so the CO concentration has to be increased to 15% to achieve 100% conversion of NO to $N_2$.

Replacing the reactant mixture over the 5% CuO/1% $CeO_2$/Ambersorb catalyst by 3% NO + 1% n-hexane at GHSV = 60 $hr^{-1}$ led to a lower conversion of NO, e.g. at 200°C about 50% NO conversion was observed with selectivities to $N_2$ and $N_2O$ of 90% and 10%, respectively [13]. The catalyst gradually deactivated. However, adding 20% $O_2$ to the reactant stream and maintaining the reaction conditions led to 100% NO conversion with unchanged product selectivity. Complete conversion of NO was maintained upon lowering the temperature step-

wise to 140°C, but the $N_2$ selectivity gradually decreased to 80% as the reaction temperature was lowered. Reducing the temperature further led to significant losses in NO conversion and $N_2$ selectivity. No deactivation of the catalyst was observed when there was $O_2$ in the reactant stream. No characterization of the oxidation state of the active components was carried.

A carbon-modified gamma alumina-supported copper oxide was recently investigated [14] in terms of the state of copper and the activity of the catalyst and compared with the unmodified catalyst. The gamma-$Al_2O_3$ was repeatedly treated with amphiphilic carbonaceous materials (ACM) (thermally treated wood tar peach resin treated with concentrated $H_2SO_4/HNO_3$ = 2/1 and then sequentially with $H_2O_2$ and methanol before dispersing in concentrated $NH_4OH$) and then impregnated by incipient wetness with a solution of basic copper carbonate/ammonium carbonate in dilute $NH_4OH$. Using a reactant mixture of NO = CO = 1200 ppm in Ar, modification of the catalyst with 17 ACM treatments reduced the light-off temperature for NO reduction by 25-35°C compared with all of the other catalysts tested, included the unmodified $CuO/Al_2O_3$ catalyst. At approximately 175°C, all of the catalysts exhibited over 90% NO conversion. It was proposed that the catalytically active complex (CAC) consisted of a finely dispersed copper oxide phase in which redox reaction occurs and that the carbon phase prevented the aggregation of this dispersed phase. At temperatures above 100°C, it was proposed that the rate determining step can be shown by Equation 3, while reaction of the catalyst with CO regenerates CAC by Equation 4:

$$2NO + CAC \rightarrow N_2 + CAC^*[O] \quad (3)$$

$$CO + CAC^*[O] \rightarrow CAC + CO_2. \quad (4)$$

The research discussed here is consistent with the rate determining step being the removal of surface oxygen species or the adsorption and dissociation of the NO reactant. Most of the studies indicate that the NO reduction reaction is produced by cations that readily undergo redox reactions and can function as oxygen transfer/storage components that depends on temperature and gas-phase composition. Addition of dopants that also can undergo redox reactions, e.g. Ce and Fe, have been shown to enhance the NO conversion and/or $N_2$ selectivity. The product selectivity is at least in part determined by the reaction temperature, where low reaction temperatures tend to favor $N_2O$ formation relative to the desired $N_2$ product. Gas-phase components such as $O_2$, $CO_2$, and $H_2O$ can inhibit the overall CO + NO reaction by competitive adsorption on the catalyst surface and by retarding oxygen removal from the surface of the catalyst.

Surface reactions involved in the reduction of NO by CO can be represented by the following reactions, but not necessarily in the sequence given:

$$NO_{(g)} \rightarrow NO_{(ads)} \quad (5)$$

$$NO_{(ads)} \rightarrow N_{(ads)} + O_{(ads)} \quad (6)$$

$$CO_{(g)} \rightarrow CO_{(ads)} \quad (7)$$

$$CO_{(ads)} + O_{(ads)} \rightarrow CO_{2(g)} \quad (8)$$

$$N_{(ads)} + NO_{(ads)} \rightarrow N_2O_{(ads)} \quad (9)$$

$$2N_{(ads)} \rightarrow N_{2(g)} \quad (10)$$

$$N_2O_{(ads)} \rightarrow N_{2(g)} + O_{(ads)} \quad (11)$$

$$2O_{(ads)} \rightarrow O_{2(g)}. \quad (12)$$

Higher reaction temperatures tend to favor Reaction 10 over Reaction 9 over Cu catalysts. At the same time, Reaction 8 tends to be a fast reaction over these catalysts.

**Part-1C**

**Part 1C** is a series of reviews centered on different types of catalysts that could be utilized for the *in situ* reduction of NO by CO in flue gases, i.e. $2CO + 2NO \rightarrow N_2 + 2CO_2$.

Supported copper-based oxide catalysts have been shown to exhibit relatively high NO conversion and $N_2$ selectivity under model laboratory conditions. It has also been demonstrated that adding Ce to Cu-based catalysts can enhance the NO reduction activity and/or $N_2$ selectivity. The Ce promoter also provides a synergetic effect with the Cu in providing tolerance of the catalyst for the presence of $O_2$, $H_2O$, and $SO_2$ in the NO + CO reactant stream. Thus, the Cu/Cu couple inhibits deactivation induced by poisons. It has been proposed that this effect results from enhancing redox couples so that redox reactions involving Cu and Ce are promoted and occur more easily and at lower temperatures. At the same time, selectivity to the $N_2$ deep reduction product of NO is promoted, which is important since the formation of undesirable $N_2O$ as a reaction product tends to be favored by low reaction temperatures. High dispersions of the active sites are required, and it has been reported that formation of ternary oxide catalysts through a hydrotalcite-type intermediate, based on the structure found in nature for $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, provides high dispersions of active components. Insight into the mechanistic steps of the redox reactions occurring in NO reduction by CO is discussed , and pertinent references are reviewed here.

***C.*** *Cerium-Promoted Copper Oxide Catalysts.* It is well-established that cerium oxide is a beneficial additive to three-way automotive catalysts [1]. It's attributes include stabilization of alumina supports against sintering, increased dispersion of noble metals, promotion of the water gas shift reaction shown in Equation 1, and storage and migration of oxygen [1].

$$H_2O + CO \;?\; H_2 + CO_2 \qquad (1)$$

With respect to CO oxidation, it was found that addition of small quantities of Ce (0.6-1.3 wt% Ce) to $Al_2O_3$ enhanced the CO oxidation activity of $Pt/CeO_2/Al_2O_3$ catalysts [2]. Higher contents of Ce and high temperature aging of the catalysts decreased the performance of the catalysts. Doping $CeO_2$ with Cu resulted in a synergetic CO reduction effect of the catalyst and an easy reoxidation of the deeply reduced ceria by $O_2$ [3]. These effects were proposed to be induced by redox processes. A study of NO decomposition on a $Co^{2+}/Ce^{3+}$ A zeolite, with 1.77 Co and 2 Ce per unit cell, showed by static and dynamic experiments that the presence of Ce promoted the activity for NO decomposition and that under static conditions the NO decomposition occurred at lower reaction temperatures than with the single component catalsyts [4]. Under static temperature programmed reaction (TPR) conditions, the principal product was $N_2$, while $N_2O$ was the dominant product under dynamic vacuum temperature programmed desorption (TPD) conditions [4].

More recently, CuO/gamma-$Al_2O_3$ and $CuO/CeO_2$ catalysts were prepared by aqueous incipient wetness impregnation and tested using a reactant mixture of 5% NO, 10% CO, and 85% He [5]. At 200°C and GHSV = 2500 $hr^{-1}$, as the Cu content of the catalyst was inceased stepwise, the $CuO/Al_2O_3$ catalyst exhibited a maximum of about 50% NO reduction when the CuO loading was 11 wt%, and the selectivity was 100% to $N_2O$. Under the same conditions, the $CuO/CeO_2$ catalyst achieved 100% NO reduction when the CuO loading was 7 wt% or higher. Upon increasing the GHSV to 5000 $hr^{-1}$, the NO conversions over the $CuO/Al_2O_3$ and $CuO/CeO_2$ catalysts decreased to 13% and 80%, respectively. In all cases, when the reaction temperature was increased to 300°C, $N_2$ was the only product observed. The overall activity of the catalysts was in the order of $CuO/CeO_2$ > $CuO/Al_2O_3$ > crystalline CuO. It was proposed that the support, especially $CeO_2$ enhanced the reducibility of the copper oxide to form dispersed $Cu^+/Cu^o$ active species.

This investigation can be compared with a study of Jurczyk and Drago with 5 wt% CuO/Ambersorb and 1 wt% $CeO_2$/5 wt% CuO/Ambersorb catalysts [6]. The catalysts were prepared by incipient wetness impregnation of metal nitrates, which were decomposed by calcination at 360°C in flowing He. The catalytic studies were carried out with 5% NO + 10%

CO in He at a *low* GHSV = 60 $hr^{-1}$. Over the 5 wt% CuO/Ambersorb catalyst, it was observed that the NO was completely converted to $N_2$ (79%) and $N_2O$ (21%) at 180°C. Addition of 1% $CeO_2$ to the CuO catalyst improved the $N_2$ selectivity to 99% at this reaction temperature.

The electrochemical behavior of Cu species in CuO, $CeO_2$, and $ZrO_2$ were studied from the viewpoint of CO oxidation and NO reduction [7]. The materials were made by a solution combustion technique, and it was shown that $Cu^{2+}$ cations were substituted for $Ce^{4+}$ to give a $Ce_{1-x}Cu_xO_{2-y}$ solid solution. It was reported that the redox potentials of the $Cu^{2+}/Cu^{1+}$ and $Cu^{1+}/Cu^{o}$ couples in the $CeO_2$ matrix were lower than those in CuO and $ZrO_2$ matrices, indicating that Cu underwent easier reduction and oxidation in the $CeO_2$ matrix. For the reactions of CO + $O_2$, NO + CO, and NO + $NH_3$ under undefined conditions, the trend of activity in all cases was 5% $Cu/CeO_2$ > CuO > 5% $Cu/ZrO_2$. Mechanistically, it was proposed that the reductant partially reduces $Cu^{2+}$ by transfer of an electron ($e^-$) to the copper, and then electron transfer on the surface of the catalyst takes place, i.e. $-Ce^{4+}--O^{2-}--Cu^{2+}-- + e^- \rightarrow -Ce^{4+}--O^{2-}--Cu^{1+}-- \rightarrow -Ce^{3+}--O^{2-}--Cu^{2+}-- \rightarrow -Ce^{4+}--O^{2-}--Cu^{2+}-- + e^-$. The released electron reduces NO. As pointed out in Report Part 1A, the electron would go into an antibonding orbital of adsorbed NO, thus weakening the N-O bond so that it is ruptured on the surface of the catalyst.

To study the synergism between Cu and Ce in oxides, catalysts consisting of (a) CuMgAlO, (b) CeMgAlO, and (c) CuCeMgAlO were synthesized by a coprecipitation method at pH = 9.5 [8]. The materials dried at 120°C exhibited X-ray powder diffraction (XRD) patterns corresponding to (a) a hydrotalcite-type (HT) structure, (b) HT + $CeO_2$, and (c) HT + $CeO_2$. After calcination at 750°C, the XRD patterns showed evidence for the presence of (a) MgO + possibly CuO and spinel, (b) MgO + $CeO_2$, and (c) MgO + $CeO_2$. Thus, the formation of CuO and spinel in the catalysts seemed to be hindered by the presence of Ce. Based on oxides, the composition of the catalysts and the observed BET surface areas are given in Table 1.

**Table 1.** Composition and Surface Areas of the Catalysts [8]

| Catalyst | Composition (wt%) | | | | S.A. ($m^2/g$) |
|---|---|---|---|---|---|
| | MgO | $Al_2O_3$ | CuO | $CeO_2$ | |
| (a) CuMgAlO | 62.0 | 29.3 | 8.4 | --- | 184 |
| (b) CeMgAlO | 60.0 | 29.0 | --- | 9.1 | 160 |
| (c) CuCeMgAlO | 56.0 | 26.0 | 7.2 | 8.7 | 169 |

The calcined catalysts were tested in a flow of 600 ppm NO + 1.4% CO + 0.5% $O_2$ in a He carrier gas; total flow rate = 400 ml/min over 150 mg catalyst [8]. At 250°C, the conversion of NO to $N_2$ over the three catalysts was observed to be (a) 11%, (b) 0%, and (c) 50%. At 300°C, the conversion of NO to $N_2$ over the three catalysts was observed to be approximately (a) 50%, (b) 0%, and (c) 85%. Adding 1% moisture to the reactants resulted in the following NO conversion levels: (a) 3%, (b) 0%, and (c) 100%. Thus, the presence of moisture in the reactant strea (m inhibited the (a) CuMgAlO catalyst, had no observable effect on the b) CeMgAlO catalyst, and promoted the (c) CuCeMgAlO catalyst. Increasing the reaction temperature of all of the catalysts to 720°C resulted in approximately 100% of the NO to be converted to $N_2$, with or without moisture being present. At this reaction temperature, adding 500 ppm $SO_2$ to the moist reactant stream resulted in rapid deactivation of the (a) CuMgAlO and (b) CeMgAlO catalysts, i.e. loss of 50% activity in 9-11 min, but no loss of activity was observed during a 50 min test of the (c) CuCeMgAlO catalyst. Therefore, the presence of both Cu and Ce in the catalyst resulted in a highly dispersed, active, stable, and poison-resistant catalyst for the reduction of NO by CO. It was proposed that Cu and Ce together gives a high concentration of $Cu^{1+}$ species and oxygen vacancies that function as adsorption sites and promotes the water gas

shift reaction (Equation 1), as well as the NO reduction reaction. The $SO_2$ tolerance of the (c) CuCeMgAlO catalyst might be due to the following reaction:

$$SO_2 + CO \rightarrow S + CO_2, \quad (2)$$

since sulfur was observed at the cool reactor outlet. However, the presence of some sulfate on the catalysts after testing was detected by XPS, with the quantities in the order of b) CeMgAlO > (a) CuMgAlO > (c) CuCeMgAlO.

The effects of $O_2$, $H_2O$, and $SO_2$ on the NO and CO conversions over these three catalysts was studied further [9], and it was observed that the presence of $O_2$ in the NO + CO reactants decreased the NO conversion slightly over the (a) CuMgAlO catalyst but slightly increased the NO conversion over the (c) CuCeMgAlO catalyst. At temperatures $\geq 550^oC$, the presence of moisture had no effect on the NO conversion. However, it significantly increased the conversion of CO under these conditions over these two catalysts, but it only slightly increased the CO conversion over the (b) CeMgAlO catalyst. At $720^oC$ and after 40 min on-stream with 500 ppm $SO_2$ added to the moist reactant stream over the (a) CuMgAlO, (b) CeMgAlO, and (c) CuCeMgAlO catalysts, a 25% loss of CO conversion over (a), a 50% loss of CO conversion over (b), and a 0% loss of CO conversion over (c) were observed. It was reported [9] that the (c) CuCeMgAlO catalyst showed no deactivation even after 24 hr on stream. It was proposed that $Cu^{2+}$ is an adsorption site for NO, while $Cu^{1+}$ is an adsorption site for CO.

***C.1.*** *Further Perspectives on Hydrotalcite-based Catalysts.* The above described (c) CuCeMgAlO active catalyst [8,9] was based on formation of the hydrotalcite structure in the dried catalyst. Upon calcination, MgO and $CeO_2$ were crystallographically identified, but the Cu and Al components were in amorphous or highly dispersed states. It has been shown that for ternary component catalysts, e.g. Cu/Zn/Al and Cu/Zn/Cr catalysts used for methanol synthesis from $H_2$/CO synthesis gas—one of the largest industrial processes today, catalysts with the "proper" composition and formed *via* a hydrotalcite-type intermediate that is subsequently calcined to oxides, appears to yield the most active catalysts [10-13]. In this case, the $Mg^{2+}$ component is replaced by $Cu^{2+}$ and $Zn^{2+}$. The ratio of the metal cations required to give a uniform hydrotalcite structure is dependant on the particular cations and their relative sizes, e.g. with Cu/Zn/Al or Cr, the molar ratio of the metal ions = 30/45/25 is ideal and gives a single-phase $(Cu_{0.4}Zn_{0.6})_6$(Al or Cr)$_2(OH)_{16}CO_3 \cdot 4H_2O$ hydrotalcite-type catalyst intermediate [13]. Subsequent calcination, e.g. at $350^oC$, gives highly dispersed catalysts.

A variety of hydrotalcite-type materials have been prepared as catalysts for the reduction of NO by CO, including Cu/Co/Al and Cu/Mg/Al [14]. Calcination of the former at 300-$600^oC$ yielded XRD evidence of the formation of a spinel-like phase, while calcinations of the latter yielded only XRD peaks of MgO. Catalyst testing was carried out with 8000 ppm NO + 8500 ppm CO in He at a flow rate of 22.5 ml/min over 50 mg catalyst. Catalysts prepared through a hydrotalcite-type precursor were more activity for NO reduction than were catalysts prepared by stoichiometrically coprecipitated samples and materials prepared by mechanically mixing the metal oxides prior to calcination. A Cu/Co/Al = 1/7/1 catalyst exhibited 100% NO conversion at $115^OC$, while at that temperature Cu/Co/Al = 1/3/1 and 1/1/1 catalysts showed about 10% and 0% NO conversion, respectively. At $200^oC$, the latter catalysts showed about 75% and 30% NO conversion, respectively, while the 1/7/1 catalyst still exhibited 100% NO conversion. It was shown that calcinations at 350-$400^oC$ gave more active catalysts than those calcined at 600 or $800^oC$. It was proposed on the basic of TPR studies and the catalytic results that the most reducible catalyst, Cu/Co/Al, was the best catalyst for reduction of NO by CO. Based on further TPD studies, the following mechanistic scheme was proposed [14] where $O_{(Cat)}$ = lattice oxygen and $V_{(Cat)}$ = an oxygen vacancy:

$$CO + O_{(Cat)} \rightarrow CO_2 + V_{(Cat)} \quad (3)$$

$$NO + V_{(Cat)} \rightarrow NO—Cat \quad (4)$$

$2(NO—Cat) \rightleftharpoons N_2O + O_{(Cat)} + V_{(Cat)}$ (lower temp.) (5)

$N_2O + V_{(Cat)} \rightleftharpoons N_2O—Cat$ (6)

$N_2O—Cat \rightleftharpoons N_2 + O_{(Cat)}$ (higher temp.) (7)

$2(N_2O—Cat) \rightleftharpoons N_2 + O_{(Cat)}$ (higher temp.) (8)

Again, very good catalyst surface redox properties are needed for high catalytic activity, which was achieved by having well-dispersed Cu and Co in the catalyst.

These mechanistic reaction steps can be compared with those proposed for the NO + CO reaction over a 10.4 wt% $Fe/SiO_2$ catalyst consisting principally of $Fe_2O_3$ supported on powdered $SiO_2$, where fast redox reactions of NO, CO, and $N_2O$ on the reduced surface, e.g. close to $Fe_3O_4$, involving atomic oxygen species adsorbed on reduced surface sites occurred [15]. The catalyst surface was proposed to be reduced by the following steps, where $O\text{-}O_{(Cat)}$ represents adsorbed oxygen species and $CO\text{-}O_{(Cat)}$ represents adsorbed CO:

$CO + O\text{-}O_{(Cat)} \rightleftharpoons CO_2 + O_{(Cat)}$ (9)

$CO + O_{(Cat)} \rightleftharpoons CO\text{-}O_{(Cat)}$ (10)

$CO\text{-}O_{(Cat)} \rightleftharpoons CO_2 + V_{(Cat)}$ (11)

$CO + O\text{-}V_{(Cat)} \rightleftharpoons CO_2 + V_{(Cat)}$ (12)

Oxidation of the catalyst was proposed to occur by the following steps:

$2NO + V_{(Cat)} \rightleftharpoons N_2O + O\text{-}V_{(Cat)}$ (13)

$N_2O + V_{(Cat)} \rightleftharpoons N_2 + O\text{-}V_{(Cat)}$ (14)

$O\text{-}V_{(Cat)} \rightleftharpoons O_{(Cat)}$ (15)

$2NO + O_{(Cat)} \rightleftharpoons N_2O + O\text{-}O_{(Cat)}$ (16)

$N_2O + O_{(Cat)} \rightleftharpoons N_2 + O\text{-}O_{(Cat)}$ (17)

CO can also adsorb onto reduced sites and then be react directly with $N_2O$:

$CO + V_{(Cat)} \rightleftharpoons CO\text{-}V_{(Cat)}$ (18)

$N_2O + CO\text{-}V_{(Cat)} \rightleftharpoons N_2 + CO_2 + V_{(Cat)}$ (19)

On prereduced catalysts, reaction steps 13 and 12 are very fast. However, reaction 18 could lead to lower steady state reaction rates. It is clear that once again, surface redox chemistry is crucial to the performance of the catalyst and that oxygen transfer and removal from the surface of the catalyst can be limiting reaction step in the reduction of NO to $N_2$.

**Part-2**

**Part 2** is a series of reviews centered on different types of catalysts that could be utilized for the *in situ* reduction of NO by CO in flue gases, i.e. $2CO + 2NO \rightleftharpoons N_2 + 2CO_2$. Activated carbon and other carbons have been investigated as direct reducing agents, as well as providing high surface area supports for alkali and transition metal catalysts, for NO reduction. Most of the studies carried out to-date have been model studies utilizing temperature programmed reaction (TPR), temperature programmed desorption (TPD), and isothermal flow experiments. Carbons do directly reduce NO, and different reactions are dominant in different temperature regimes. At lower reaction temperatures, the surface of the carbons tend to become oxidized, and the NO reduction reaction is retarded because of the inability of NO to chemisorb/react on the oxidized surface. Indications are that CO removes oxygen from the carbon surface and promotes the reduction of NO. Under some reaction conditions, the presence of $O_2$ in the reactant mixture promotes NO reduction (significantly so at higher temperatures and when catalysts are present), while the presence of moisture tends to inhibit the reaction, particularly by competitive adsorption at lower reaction conditions.

Fresh chars and carbons tend to be more reactive for NO reduction (and carbon oxidation) than high temperature stabilized activated carbons. This is apparently due to the "amorphous" surface carbon/residues, which are probably lower molecular light materials, and the fresh materials suffer higher carbon burnoff than do the activated carbons. Highly activated

materials that have been pyrolyzed or otherwise thermally treated at high temperatures usually require appreciably higher temperatures for NO reduction, even when catalysts are impregnated into the carbons. However, dispersed metal catalysts tend to enhance higher NO reduction at lower temperatures over most carbons, as well as higher carbon burnoff. High dispersions of the active sites are required, preferably on the surface of high surface area carbons. The presence of CO in the reactant gas mixture aids in the reduction of NO, again in a temperature dependent manner. The simultaneous presence of catalysts on carbon supports and CO in the reactant gas mixture can greatly promote the reduction of NO in a gas stream.

Insight into the mechanistic steps of the redox reactions occurring in NO reduction by CO is discussed, and pertinent references are reviewed here. The focus is on the role of carbon as reducing agent and the promotion of NO reduction by metal catalysts and CO in the reactant mixture.

***A.*** *Carbon Reduction of NO*. Various carbons have been investigated as a reducing medium for NO conversion to $N_2$. The carbons include activated carbons prepared from many different materials, graphite, and "chars" prepared from coals or polymers, especially phenol-formaldehyde resin. The terms "carbons" and "chars" are sometimes used interchangeable. Using only carbons as prepared, the carbon is the reducing agent and is consumed in the reduction of NO, e.g. as represented in Equation 1.

$$C^* + 2NO \rightarrow CO_2 + N_2 \qquad (1)$$

Carbons and chars can naturally contain other moieties such as alkali/alkaline earth metals and transition metals usually in an oxidized or sulfided state. It is sometimes difficult to separate the effects of carbons in reducing NO from the effects of catalysts.

Studies of the kinetics of the NO-carbon reaction were reviewed in 1997 by Aarna and Suuberg [1]. The review is well-referenced, and the references will not be repeated here. It was pointed out that the key variables affecting the kinetics of NO reduction over carbons are temperature and NO partial pressure. With fairly pure, highly heat-treated carbons, it was concluded that there were three distinct reaction regimes defined by the reaction temperature. At temperatures extending from ambient temperature up to about 200-225$^o$C, reversible and irreversible chemisorption processes occur and steady gasification is not possible. In the "low temperature" regime range of about 225-725$^o$C, gasification occurs and is characterized by low activation energies. At temperatures above about 725$^o$C, gasification occurs with high activation energies. The "break-point" between these two temperature regimes is located between about 575 and 800$^o$C, depending on the particular carbon being gasified. Graphite, with low surface areas, tend to give high apparent activation energies, e.g. 200-240 kJ/mol. High surface area carbons and chars tend to give appreciably lower apparent activation energies, e.g. 35-70 kJ/mol in the low temperature gasification regime and 120-160 kJ/mol in the high temperature regime. In reaction studies of *pure* NO with carbons in the gasification temperature ranges, the order of reaction with respect to NO is approximately 1, while the order is about 2 in the low-temperature chemisorption regime. A first-order heterogeneous NO reduction rate expression may be represented by

$$r = -k \cdot C_{NO}, \qquad (2)$$

where r is the molar NO reduction rate per unit gas volume, k has units of reciprocal time, and $C_{NO}$ is the molar concentration of NO. The conversion in a fixed-bed reactor would then be given by

$$k \cdot t = -\ln(1 - f_{NO}), \qquad (3)$$

where t is the residence time and $f_{NO}$ is the fractional conversion of NO.

Chars from coal and petroleum sources tend to contain mineral impurities, and the temperature "break" in the activation energies curves were generally not observed with these

materials. In addition, there was no consistent variation of activation energy with coal rank, surface area of the carbon, NO partial pressure, or reactivity. Utilizing all literature data sets (24 different carbons/chars), a mean apparent activation energy of 133 kJ/mol was obtained. The expression for the rate constant, given in units of $[g_{NO}\ m^{-2}\ (h \cdot atm_{NO})^{-1}]$, resulting from the averaging procedure was represented as

$$k = 5.5 \times 10^{6} \exp(-15{,}939/T), \quad (4)$$

where T is the temperature.

It was observed that the apparent order of NO reduction at the gasification temperatures was strongly influenced by the presence of CO in the reactant gas stream, where the CO may be generated *in situ* as a product of gasification. The presence of CO enhances the reduction of NO. The CO might fulfill two roles in NO reduction; (A) removing surface oxides from the carbon surface, C(O), to expose free reactive carbon sites, C*, and (B) direct reduction of the NO by reaction, i.e.

$$\text{(A)}\ CO + C(O) \rightarrow CO_2 + C^* \quad (5)$$

$$\text{(B)}\ 2CO + 2NO \rightarrow 2CO_2 + N_2. \quad (6)$$

In the latter case, the carbon could be acting as a catalyst for the NO reduction. It is noted that both CO and $CO_2$ are observed as product gases resulting from the NO-carbon reaction. Generally, more $CO_2$ is formed at low gasification temperatures such that the $CO/CO_2$ ratio <1. As the reaction temperature increases, the $CO/CO_2$ ratio monotonically increases so that CO is the prevalent carbon oxide. However, the ratio decreases with increasing residence time, indicating that CO undergoes a sequential reaction, e.g. *via* reactions 5 and/or 6.

Empirical studies have been carried out in which CO was added to the feed gas, and it was observed that at high concentrations of CO, e.g. in the % range, the reaction order of the surface-catalyzed reduction of NO by CO ranges from 0.18 to 0.43 in NO and from 0.38 to 0.53 in CO. However, at CO concentrations of =700 ppm, the CO dependence approaches zero order.

With respect to other gases in the reactant stream, it has been reported that the NO-carbon reaction is inhibited by the presence of water vapor. On the other hand, the presence of oxygen enhances the rate of NO reduction, especially in the presence of catalysts in the carbons.

In studying the low temperature chemisorption and higher temperature desorption of NO and $O_2$ on carbons and the kinetics of the formation of surface complexes, it was reported that NO reacts *via* a second order reaction, e.g. it might be represented formation of a NO dimer in a pore that reactions with two C* sites to form $N_2$ and two C(O) complexes as

$$2NO \rightarrow O{=}N\cdots N{=}O \quad (7)$$

$$C^*\cdots O{=}N\cdots N{=}O\cdots C^* \rightarrow N_2 + 2C(O). \quad (8)$$

In this reaction sequence, there is no surface nitrogen intermediate. In the presence of $O_2$, this reaction might be inhibited, and NO may react with the oxidized carbon surface to form adsorbed $NO_2$ that is difficult to desorb. The $NO_2$ complex may also slowly regenerate the NO. In either case, the active C* site will be blocked, leading to low levels of NO conversion unless the carbon surface is "cleaned" by another mechanism such as "oxide" removal by reaction with CO or other reagent.

The role of CO in the NO-carbon reaction has been consider further over graphite, Wyodak subbituminous coal-derived char, and a phenolic resin char [2]. It appeared that Reaction 6 occurred in parallel with gasification Reactions 1A and 1B. The rate of

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \quad (6)$$

$$C^* + 2NO \rightarrow CO_2 + N_2 \quad (1A)$$

$$2C^* + 2NO \rightarrow 2CO + N_2 \quad (1B)$$

Reaction 6 was sensitive to the nature of the oxide content on the carbon surface and was characterized by an activation energy around 116 kJ/mol in the temperature range of approximately 500-850°C (with NO ~ 65 ppm and CO = 270-400 ppm in He). In this

temperature range, CO was zero order while NO was first order. The order for NO could not be determined at lower temperatures since the NO-carbon reaction does not have a unique order and kinetic analyses are complicated by surface oxides deposited by oxidizing gases. It appears that the CO rate enhancement does not involve simple Reaction 5 of surface oxide stripping to expose reactive sites, but rather involves an unclarified carbon-surface-catalyzed reaction of NO with CO [2]. The resin char used here was a low surface area (50 $m^2$/g) microporous material, and at high reaction temperatures (>675$^o$C) it appears that mass-transfer limitations were playing a role in the rate of NO conversion. However, there was no evidence for such limitation for the low surface area graphite nor for the mesoporous coal-derived carbon.

While the specific nature of the active surface sites for NO reduction has not been clarified, empirical insight has been provided in the role of CO on promoting the reduction of NO. The role played by the presence of $O_2$ is temperature dependent and may be greatly affected by the presence of catalysts. In general, mass transfer limitations are not significant with porous catalysts, and high surface areas of the carbons are beneficial.

***B.*** *Reduction of NO by Catalyst-Promoted Activated Carbons*. A particularly intenstive series of studies on NO reduction by catalyst-promoted activated carbons has been carried out by Illán-Gómez and coworkers. These involve high surface areas carbons, e.g a coal-derived activated carbon that had a $N_2$-BET surface area of 2087 $m^2$/g and a $CO_2$-BET surface area of 1080 $m^2$/g [3]. Upon doping the coal-derived carbon with $K^+$, *via* KOH or $CH_3COOK$, promotion of significant reduction of NO was found to occur at considerably lower temperatures [4,5], whether the $K^+$ was added by ion exchange [4] or by impregnation [5]. Using NO chemisorption, temperature-programmed reaction (TPR), temperature-programmed desorption (TPD), and flow reaction studies, three characteristic reactivity regions were found with activated carbons containing 2.8, 4.6, and 7.4 wt% K [5]. These regions were the following:

A. high catalytic activity at low temperatures due to dissociative NO chemisorption, accompanied by $N_2$ and $N_2O$ evolution and oxygen accumulation on the catalyst surface,
B. severe catalyst deactivation at intermediate temperatures as the catalyst became fully oxidized, and
C. recovery of high catalytic activity at high temperatures as the catalyst was reduced by carbon, accompanied by the evolution of CO and $CO_2$.

As the K loading was increased, the region of high activity at low temperature was extended. The results were consistent with Reactions 7 and 8 for formation of $N_2$, accompanied by the reaction represented by Equation 9,

$$C^{*}\cdots O{=}N\cdots N{=}O\cdots C^{*} \;?\; N_2O + C(O) + C^{*}, \qquad (9)$$

where surface N species, C(N), were not formed. Potassium was found to be very active in dissocating NO, even at temperatures as low at 60$^o$C. It was proposed that this is due to $K^+$ being reduced by the carbon substrate and promotion of surface redox reactions.

Carbons derived from coal, a phenol-formaldehyde polymer resin, and almond shells were promoted by ion exchange with $Ca^{2+}$ to levels of 1.9, 3.6, and 0.6 wt%, respectively [6]. Chemisorption and kinetic experiments were carried out at atmospheric pressure using a 0.4% NO/He gas mixture. It was concluded that Ca catalyzes NO reduction by carbon through a mechanism that is consistent with the formation of intermediate CaO(O) surface species. However, these species are much less effective in chemisorbing NO than "reduced" potassium species, resulting in much less oxygen being transferred to the carbon active sites. The results also showed that the porous structure and the surface chemistry of the carbons determined, in a complex way, the catalyst loading and dispersion and the catalyst/substrate contact, controlling the catalytic activity of Ca in NO reduction. Adding $Ca^{2+}$ in excess to that incorporated by ion

exchange resulted in decreased NO conversion, analogous to the effect observed for Ca-catalyzed gasification of C with $CO_2$.

Similarly, a coal-derived, microporous, high surface area (1790 $m^2/g$), activated carbon was promoted with $Fe^{3+}$ by (a) precipitation of a-FeOOH, (b) precipitation of ß-FeOOH, and (c) impregnation with $Fe(NO_3)_3$ solution [6]. Iron was found to catalyze NO reduction by carbon through a redox mechanism similar to that observed for the K-and Ca-catalyzed reaction. However, the Fe species present on the carbon surface before NO reduction ($Fe_xO_y$ or FeO) were less effective than the previously studied K-species. By analogy with the K-and Ca-catalyzed NO reduction reaction, the catalyst/carbon interface and interfacial area were the determining factors in whether the oxygen transfer from the catalyst to carbon and regeneration of the reduced catalyst occurred efficiently. It was observed that as Fe particle size increased, the catalyst/carbon interfacial or contact area decreased, resulting in a less effective transfer of oxygen derived from the NO from the catalyst to the carbon.

Portions of the same coal-derived activated carbon were also impregnated with excess aqueous solutions of Cr, Fe, Co, Ni, and Cu nitrates to give loadings of 2.0, 4.7, 3.7, 3.5, and 3.0 wt%, respectively [8]. After thermal treatment in He that consisted of heating to 900°C at a rate of 50°C/min, exposure to air, and analysis by X-ray powder diffraction, metallic particles of Co, Ni, and Cu were observed with crystallite sizes of 6, 3, and 7 nm, respectively. Iron oxide particles of ?-$Fe_2O_3$ were observed, while no diffraction peaks were observed with the Cr-containing sample. All of the transition metals catalyzed the NO-carbon reaction (studied in the absence of $O_2$), causing a decrease in the activation energy and substantial shifts of the NO reduction curves toward lower temperatures. Again, the TPR curves, the reactivity data with a 0.4% NO/He reaction mixture, and the product composition distributions support a redox mechanism involving different oxidation states of the metals and the carbon matrix. At low reaction temperatures (<400°C), Fe, Co, and Ni are the most effective catalysts, which is consistent with their abilities to chemisorb NO dissociatively. At high reaction temperatures (500°C), Cu, Co, and Ni exhibit the highest activities. These observation indicate that at low temperatures, the controlling step in the process is NO chemisorption, whereas at high temperatures reduction of the intermediate oxidized metal species is the rate-limiting step in the reaction sequence. At low reaction temperatures, all of the transition metals were much less active in promoting the NO-carbon reaction than was K (in terms of mol NO reduced/mol of metal/sec). However, at 500°C the Cu catalyst was more reactive than the K catalyst, and Co and Ni were approaching the activity of the K promoter.

The results of the previously discussed studies were summarized [9], principally in terms of TPR results, and it was pointed out that the K catalyst showed a high NO removal capability at about 200°C and achieved 100% NO reduction at 500°C. The transition metal catalysts exhibit differing behaviors because of their difference redox properties. Mechanistically and kinetically, it was proposed that the only significant reactions involving NO are the following:

$$NO + 2S \rightarrow S(N) + S(O) \quad (10)$$

$$2S(N) \rightarrow N_2 + 2S \quad (11)$$

$$S(N) + NO \rightarrow N_2O + S \quad (12)$$

where S = C* or a reduced metal species. At low temperatures, catalyst deactivation is observed because of oxygen accumulation on the surface *via* reaction 10. For the catalysts, the transfer of oxygen from the oxidized catalytic site, S(O) shown in Equation 13, to the carbon is proposed to be crucial for maintaining high steady-state catalytic activity. This is facilitated by a large interfacial area of catalyst/carbon contact, which is

$$S(O) + C^* \rightarrow C(O) + S \quad (13)$$

related to high dispersion of the catalyst on the carbon surface. After regeneration of the reduced catalyst site, the remaining kinetically significant reaction the same as those observed for the oxygen-carbon reaction:

$$2C(O) \rightarrow CO_2 + C^* \quad (14)$$

$$C(O) \rightarrow CO_{(g)} \quad (15)$$

It was pointed out [9] that the practical challenges are to (a) minimize carbon consumption (i.e. maximize Reaction 14 but minimize Reaction 15), (b) maximize NO chemisorption (i.e. maximize Reaction 10), and maximize the rate of oxygen transfer (e.g. by Reaction 13). These challenges can be met by catalyst selection and maximizing the dispersion of the catalyst on the carbon surface. It is noted, however, that Reaction 15 might be a beneficial reaction because the CO can remove oxygen from the surface to form $CO_2$ (see Equation 5) and could enhance reduction of NO (see Equation 6).

The effects of $K^+$ on NO reduction over five coal-derived chars were examined in detail [10], where the chars were obtained from two lignites, two subbituminous coals, and a hvA bituminous coals. In addition, an almond shell-derived char, a polymer-based activated carbon, and an activated carbon obtained by chemical activation of a bituminous coal were also utilized. The chars were obtained by slow pyrolysis under $N_2$ using a heating rate of $5^oC$/min and holding at 500-900$^o$C for 2 hr. Some of the chars were also then water-washed. Studies were carried out using 0.5% NO/AR and 0.5% NO/5% $O_2$/Ar gas mixtures. It was observed that the most important reaction below 200$^o$C was adsorption of NO onto the carbon, while above 200$^o$C NO reduction by the char begins with the formation of $N_2$ and $CO_2$. The most active coal chars for NO reduction were obtained by pyrolysis at 900$^o$C followed by treatment with aqueous KOH using a KOH/coal wt ratio of 0.5/1.0.

A study of monometallic K, Fe, Co, Ni, and Cu catalysts on activated carbon was subsequently carried out [11]. The activated carbon was prepared from a hvA bituminous coal and impregnated with aqueous KOH. The coal was activated by slurrying with strong aqueous KOH solution, pyrolyzing under $N_2$ by heating at $5^oC$/min to 500 or 700$^o$C, cooled and washed several times with 5 M HCl, and then washed with distilled water [11,12]. The activated carbon was then impregnated using excess solution to obtain a metal loading of about 5 wt%. It was reported that the metal catalysts were ineffective at temperatures lower than about 200$^o$. However, at higher temperatures all of the metals catalyzed the NO reduction reaction, and the total activity was the result of two factors, the tendency of the metal to be oxidized by NO and the easiness of the resulting oxide to be reduced by carbon. The Cu and Co catalysts exhibited the highest NO conversion at 300$^o$C and the lowest temperatures for significant NO reduction to be observed. However, these two catalyst exhibited the highest burnoff of the carbon (at 300$^o$C), some 2-3 times higher than observed for the Ni, Fe, and K catalysts. However, the latter three catalysts exhibited lower NO reduction levels than the Cu and Co catalysts.

The effect of Fe, as well as Na [13] and Ca [14], on coal chars was studied further, where the char was prepared from a demineralized Chinese lignite [13,14]. Analogous to previously discussed studies, model TPR and isothermal flow reaction studies were carried out. Before testing, the chars were subjected to a 850$^o$C treatment for 30 min in an Ar atmosphere. With 1 wt% metal loadings (achieved by aqueous impregnation), the Na- and Fe-promoted chars achieved 60% NO reduction from a 500 ppm NO/Ar gas mixture at about 675$^o$C (same observed with a 2 wt% Fe sample), while the metal-free char didn't achieve this level of NO conversion until about 830$^o$C. Over the Fe catalyst, 100% NO reduction was attained at about 750$^o$C, while the complete NO conversion was not observed over the Na-promoted char until about 830$^o$C. When the pretreatment Ar was replace by the NO/Ar mixture at 700$^o$C for the Fe-char, deactivation from about 98% NO reduction to 83% in the first 15 min on-stream and then more gradually deactivation to 75% NO reduction over the next 85 min was observed. For the Na-

char, the initial 86% NO reduction declined to 60% in the first 15 min and then to 45% at the end of 100 min on-stream. Maintaining a metal loading level of 1 wt% but impregnating with both Na + Fe in varying wt ratios, it was found that the Na/Fe = 0.5/0.5 and 0.67/0.33 materials were more active (60% NO reduction observed at ~610°C) and exhibited less deactivation than the single-promoted chars and catalysts with other Na/Fe ratios.

With a 2 wt% Ca-promoted char treated in the same way, 60% NO reduction was observed at 750°C (compared to about 675°C for Fe) [14]. Addition of 1800 ppm CO to the reactant stream reduced these temperatures by 75°C and 200 °C, respectively. Under steady-state isothermal conditions at 700°C, addition of the same concentration of CO to the reactant stream increased the NO reduction from about 58% to 95% for the Fe-char, as compared with the increased from ~20% to ~50% with the Ca-char. Similarly, addition of 0.2% $O_2$ to the NO/Ar reactant mixture at the same temperature significantly increased the NO reduction over the Fe-char, i.e. from 59% to 82%, while the promotion was much less over the Ca-char, i.e. from ~20% to ~30-35% [14]. The latter promotion was even less than that observed over the unpromoted char, i.e. the oxygen promotion was from ~11% to ~35%, and it was proposed that the low oxygen promotion of the Ca-char was due to formation of inactive $CaCO_3$ on the char.

More recently, deposition of bimetallic catalysts on carbon supports and model studies of NO reduction by the carbon have been carried out [15,16] because none of the previously studied carbon-supported monometallic catalysts yielded high NO conversion activity *and* high selectivity to $N_2$. The activated carbon was prepared from a hvA bituminous coal as described above [11,15,16]. The treated coal was then sequentially impregnated with metal nitrate solutions to yield loading of approximate 3 wt% K and 4-5 wt% of Fe, Co, Ni, or Cu [15]. TPR and isothermal reactions were carried out in a fixed bed flow reactor using a 0.5%NO/5% $O_2$/He mixture. It was found that all of the transition metals promoted the K-carbon system and exhibited a synergetic effect, in particular the temperature for NO reduction was reduced, i.e. to the 200-250°C range, and the $N_2$ selectivity was nearly 100%. Among the metals analyzed, it was stated that the KNi catalyst was the most interesting because it combined a high NO reduction activity at low temperatures with the lowest loss of carbon by combustion.

The bimetallic catalysts were investigated further for NO reduction using isothermal reactions at 300°C and TPR up to 500°C with a 0.5%NO/5% $O_2$/He gas mixture, with a principal goal being to reduce carbon consumption by oxidation [16]. It was reported that KNi, NiCo, and NiCu catalysts promoted NO reduction, but the amount of catalyst on the carbon "only lightly" affected the amount of NO reduced, e.g. at 300 °C and after 2 hr on stream, a K/Ni = 3.0/4.0 wt% catalyst exhibited 89% NO conversion while a K/Ni = 1.0/0.9 wt% catalyst exhibited 65% NO conversion. The Ni/Co = 1.0/1.0 and Cu/Ni = 0.9/0.7 wt% catalysts exhibited about 75-80% NO conversion after 2 hr and a faster approach to steady-state conversion than the KNi catalysts. The NiCu catalyst was reported to yield the best performance at 250°C by showing a high NO conversion and selectivity, high $N_2$ product selectivity, and absence of $N_2O$ and CO in the reaction products.

*Reactivity of carbons and chars.* The terms "carbons" and "chars" are often used interchangeably, but they can vary in contents of impurities and in thermal treatments. Carbons are often treated at high temperature for appreciable times to "stabilize" the carbons [17], e.g. at >1000°C for =1 hr in an inert gas atmosphere. It is well-known that following carbonization, char samples contain a certain amount of highly reactive amorphous material, as a result of tar deposition and decomposition [17,18]. It has been pointed out that cellulosic chars typically exhibit high NO reduction activity, and this may be due to cellulosic chars not undergoing a high temperature stabilization treatment and containing a high degree of amorphous surface carbon.

It was also stated that it is well-known that for most char-gas reactions, very high transient reactivity is almost always observed [17]. This is due to a variety of factors, including

the variation in oxygen surface complex content during the establishment of steady-state conditions, initial enhanced reactivity due to high concentrations of dangling surface bonds, disordered surface carbon, etc. In fact, very high initial reactivities of up to 2-6 times the eventual steady-state values have been observed [3], which were typically achieved after about 80 min [17]. For stabilized carbons, NO reactivity (in terms of micromole NO/g catal/sec), e.g. at 600°C with 0.4 kPa NO, correlates well with the surface area of the carbons.

***C.*** *Reduction of NO by Potassium-Promoted Coal Briquettes*. A study was carried out using 2.00-2.83 mm particles obtained from crushed K-containing briquettes that were prepared from a Spanish hvA bituminous coal for NO reduction at 300 and 350°C [19]. Mixtures of 0.5% NO/He and 5% $O_2$/He were utilized to obtain the reaction gas mixture. It was observed that the K-containing coal briquettes improved the performance of the original char by (1) increasing the NO conversion, (2) decreasing the $CO/CO_2$ ratio in the evolved products, and (3) enhancing the selectivity toward the NO reduction against oxygen gasification. A surface enrichment of K species was observed for the most selective briquette. Therefore, a washing step in the preparation process is not beneficial because it decreases the selectivity for NO reduction, as well as increasing the carbon gasification process. A good preparation procedure for the briquettes was to slurry the coal with a KOH/humic acid mixture and then dry at 110°C before forming the briquettes, which were then pyrolyzed under $N_2$ for 2 hr at 700°C.

***D.*** *Conclusions from Studies of NO Reduction Over Activated Carbons and Carbon-Based Catalysts*. The Abstract summarizes the conclusions obtained from review of the recent research literature that is focused on model studies of the adsorption/desorption/interaction of NO with vary carbons and the level of NO reduction achieved in simple gas mixtures over carbon-supported metal catalysts. Carbons are active support materials for the reduction of NO in gas streams. Without the presence of catalysts, temperatures higher than 500°C are needed. However, supporting base metal catalysts and/or redox transition metal catalysts on the carbon supports reduced the temperature required for NO reduction. However, the thermal treatment in obtaining the activated carbon or char can greatly affect the temperature that is needed to obtain significantly high levels of NO reduction. The presence of carbon monoxide and oxygen in the reactant stream both promote the reduction of NO. In addition, the simultaneous presence of catalysts on carbon supports and CO in the reactant gas mixture can greatly promote the reduction of NO in a gas stream.

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